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Quantum confinement in Si nanocrystals

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The electronic structure of nanocrystalline Si which shows visible photoluminescence is calculated using the density-functional approach for finite structures. Except for geometry this is the same theory as for first-principles band structures of semiconductors and other solids. Our results for clusters ranging up to 706 Si atoms suggest that the band gap scales linearly with L^{-1}, where L is the cluster diameter. For such clusters it is found that dipole transitions across the gap are symmetry allowed. The finite structures thus show a direct band gap which is considerably larger than the one of bulk silicon. For larger clusters we find a strong decrease of oscillator strength, consistent with the occurrence of the indirect gap in the bulk limit.

The recent discovery of visible photoluminescence from small silicon structures in anodically etched porous silicon[1,2] has greatly increased interest in these particular kinds of fine structures, as well as in small semiconductor particles[3,4] where the same effects have been observed. An exciting perspective of this discovery is that light-emitting devices based on this effect appear feasible within the well-established silicon technology. To understand this effect, knowledge about the band structure of fine silicon structures is required. In particular, questions to be addressed are whether silicon can become intrinsically a "direct" semiconductor when in nanocrystalline clusters (or "porous") and if quantum confinement can modify the energy gap such that visible light is produced as experimentally observed. Our previous work[5,6] has dealt with quantum confinement in small silicon particles on the basis of density-functional studies. The principal result has been that an energy gap in the visible range should occur intrinsically for small particles of a few nm in diameter. Our present work shall give a more detailed account of the theoretical findings, with due attention paid to the role of the self-energy correction to the gap and to the oscillator strength as a function of particle size. In the meantime, other work based on first-principles calculations for the quantum-wire geometry has appeared,[7,8] where the conclusions concerning the intrinsic gap widening are consistent with our results. Although a controversy has arisen whether the observed effect is due to quantum confinement, as originally proposed, or whether visible photoluminescence is due to an extrinsic effect because of the unbiquitous presence of siloxenelike compounds,[9] the focus of interest in the present work is on the fundamental question whether quantum confinement in fine silicon structures can lead to symmetry-allowed optical transitions across the gap with an energy in the visible range. As the content of this work definitely shows, three-dimensionally confined silicon particles have symmetry-allowed optical transitions across the gap. In the case of periodic crystal structures, this property is termed direct gap. Moreover, this work shows that the gap widens such that particles in the experimentally reported size range produce visible luminescence.

In view of the relevance of small particles to the visible luminescence of silicon,[3,4] here we consider nanocrystals which have small dimensions in all three directions; this kind of system may be called a quantum dot. The intrinsic properties of such clusters are expected to be obtainable from the most symmetric class of such clusters, disregarding any lattice contractions. As an idealization it is assumed that these nanocrystallites are spherical with no relaxation of the bulk lattice. There are two kinds of such clusters with T_d symmetry for Si, one with a Si atom at the center and one with a tetrahedral interstitial at the center. Since our interest is in states around the band gap, saturation of all dangling bonds at the surface is essential; otherwise the gap would be completely masked by the dangling-bond states. Saturation of the dangling bonds removes the corresponding localized surface states from the energy range near the Fermi energy. Contour plots of the orbitals around the gap show no sign of hydrogen admixture; these orbitals resemble the corresponding bulk orbitals but with a smooth fall off toward the surface. Physically the dangling bonds would suppress the luminescence. We have chosen to saturate the dangling bonds with hydrogen as a most simple model for actual surface coverage.

Idealizations assuming a point-group symmetry are consistent with the finiteness of the sample. It is illustrative to discuss briefly finite clusters in the context of k-space representations implying a translational repetition of the nanocrystals, i.e., a supercell model. The Brillouin-zone folding allows a mixing of the k-space representations of the bulk crystal. The large fraction of space which remains empty for isolated nanocrystals necessarily presents a large perturbation and thus leads to a significant mixing. In the dilute limit the folded Brillouin zone shrinks to zero and only direct band gaps remain. On the other hand, the transition from the highest occupied to the lowest unoccupied orbital in a finite-cluster model may or may not be symmetry allowed.

It is useful to consider scaling of energies with the size L of the nanocrystals. Electrostatic energies scale with

$1/L$. Kinetic-energy scales with $(1/L)^2$. This would suggest a Taylor expansion for the energy as a function of $1/L$: $E(1/L)=E_0+E_1(1/L)+E_2(1/L)^2$. However, finite structures have discrete levels. As a consequence $E(1/L)$ describes only a mean scaling on which discrete jumps of an average size scaling with the average level separation $(1/L)^3$ are superposed. Earlier work on semiconductor crystallites[10] suggests that in this size range excitonic correlation effects are less important than confinement effects.

The density-functional (DF) theory which we are applying here at the level of its standard local (LDF) approximation offers itself for describing this idealized model for silicon quantum dots, since this theory is capable of describing molecules and bulk with similar accuracy.

For a discussion of absorption and luminescence, we are led to study excited states. Electronic excited states of many-electron systems pose inherent difficulties, related to the fact that excited states must meet orthogonality conditions for all lower states. The density-functional theory was originally designed to efficiently calculate ground states. Meanwhile, a number of methods have also been developed to calculate excited states from the DF formalism; for a review, see Jones and Gunnarsson.[11]

A first question relating to the meaning of DF eigenvalues ϵ_k has been solved by Janak,[12] proving that

$$\epsilon_k=\frac{\partial E}{\partial n_k} ,$$

where E is the analytical continuation of the total energy of the system to noninteger occupation numbers n_k of the Kohn-Sham orbitals.

In many instances, excited states of interest differ in symmetry from the ground state. In that case such an excited state can be the lowest state for that other symmetry, which is again accessible to a ground-state variational principle.[13] This approach, sometimes called ΔSCF (where SCF denotes self-consistent field), can also be applied to approximate functionals. It has also been used with good success for cases where the excited state does not qualify for the argument.

In finite clusters and molecules, ΔSCF with LDF is known to typically yield better than 1-eV accurate predictions for various kinds of optical excitations. For continuous functionals of the density applied to infinite systems, the single-particle excitation spectrum would coincide with the eigenvalue spectrum. In that perspective, DF band structures have an immediate meaning as an approximation to the true spectrum. The statement on the accuracy of calculated excitation energies still holds true for the bulk. However, because the semiconductor band gaps are of the same order, the fractional accuracy is too low to be very useful for excitations in bulk semiconductors. For a more accurate calculation of excited states, functionals which go beyond the LDF are needed.

Many-body calculations for bulk semiconductors have been one with the so-called *GW* (Green's function, dynamically screened interaction) approximation.[14,15] This approach leads to significant self-energy corrections to excited states. Energy-gap and dispersion relations are obtained which are in good agreement with experiment. It was found[15] that the effective ground-state potential corresponding to the *GW* self-energy is in excellent agreement with the LDF effective potential. The main effect of the nonlocal self-energy is to introduce a discontinuity, shifting the conduction bands of Si up by about 0.6 eV. This shift with respect to a LDF band structure of bulk Si is constant to better than 0.1 eV across the Brillouin zone.

On the basis of the foregoing considerations on excited-states energies, it is appropriate in the present investigation to represent the effect of the self-energy by a constant shift independent of particle size. As already mentioned, a shift of 0.6 eV results from the *GW* self-interaction corrections which leads to a gap within 0.1 eV of the experimental value for bulk silicon. On the far other end of the particle size range, connection can be made with the ultraviolet spectra of silanes which are available up to pentasilanes. We have calculated the linear pentasilane Si_5H_{12} and obtained a lowest optical excitation energy of 5.5 eV when including a self-energy correction of 0.6 eV. For the spherical pentasilane cluster, the lowest calculated excitation energy is 6.3 eV. Experimental excitation energies[16] for linear, branched, and neopentasilane are 5.8, 5.8, and 6.5 eV, respectively. These data establish that our first-principles calculations agree reasonably well with optical excitation energies on both ends of the Si particle size spectrum.

Optical transitions between the highest occupied and the lowest unoccupied orbitals are allowed in a cluster of sufficiently low symmetry. In the limit of bulk Si such transitions are forbidden because of the indirect band gap. Only the symmetry breaking by the phonons makes such transitions weakly allowed, which leads to the weak band-gap photoluminescence of bulk Si.

We have solved density-functional equations for a series of spherical Si crystallites shown in Table I using the DMOL program.[17,18] In order to facilitate the largest calculations, we have used a relatively small basis set using a single, numerically exact, atomic LDF *s* function on the saturating hydrogen atoms and frozen-core approximation with a double set of numerical functions on the Si atoms. This basis set yields excellent values for the gap energy for medium clusters, where comparisons to more accurate basis sets can be made. For very small clusters like pentasilane and smaller, the relative importance of the wave-function tails has required the use of more flexible basis sets. The potential representation includes quadrupoles for Si and dipoles for H in reasonable consistency with the truncation of the basis set. Self-consistent calculations have been done expediently, making full use of symmetry by reducing the Hamiltonian to block diagonal form and evaluating the integrals only over the asymmetric wedge containing $\frac{1}{24}$ of the full cluster in the present case of global tetrahedral symmetry.

For the excitations of interest here, the eigenvalue spectrum gives an excellent account of excitation energies obtained with ΔSCF procedures. Even for the smallest cluster, the monosilane, the agreement between the two types of calculations is better than 0.1 eV. This is so because only minor charge rearrangements occur between ground and the low excited states.

For a discussion of luminescence intensity one needs transition matrix elements or oscillator strengths, which we evaluate in **r** form:

$$f_{i,j}=\frac{2m}{\hbar}\omega_{i,j}\left\{\int \phi_j^*(\mathbf{r})x\phi_i(\mathbf{r})d^3r\right\}^2 .$$

Since only relatively few transitions near the gap energy are of interest, we can do without explicit group-theoretical decomposition of product representations. Rather, we calculate all matrix elements in a specified energy range without using symmetry. The integration scheme used for self-consistency[17] is extended over all space and the eigenfunctions are reconstructed on the integration points. The calculation of matrix elements at this level of sophistication represents a small part of the overall computational expense.

TABLE I. Clusters with symmetry of levels at the top of the valence band (Γ_v) and the bottom of the conduction band ($\Gamma_{c1}\cdots\Gamma_{c3}$). $N_{\mathrm{tot}}=N_{\mathrm{Si}}+N_H$.

N_{Si}	N_{tot}	Γ_v	Γ_{c1}	Γ_{c2}	Γ_{c3}
		Atom-centered clusters			
1	5	t_2			
5	17	t_2	a_1	t_2	
17	53	t_1	a_1	t_2	a_1
29	65	t_2	e	a_1	t_2
35	71	t_2	e	a_1	t_2
47	107	t_2	t_2	a_1	e
71	155	t_2	a_1	t_2	e
87	163	t_2	a_1	t_2	e
99	199	t_2	e	t_2	a_1
123	223	t_2	e	a_1	t_2
147	247	t_2	a_1	t_2	e
159	283	t_2	a_1	t_2	e
167	291	t_2	a_1	t_2	e
191	339	t_2	a_1	t_2	e
239	435	t_2	a_1	e	t_2
275	447	t_2	a_1	t_2	e
281	453	t_2	a_1	t_2	e
293	465	t_2	a_1	e	t_2
329	525	t_2	a_1	t_2	e
357	561	t_2	e	t_2	a_1
		Clusters centered on T_d interstitial			
4	20	t_1	a_1	t_2	a_1
10	26	t_2	e	t_2	t_2
22	62	t_2	a_1	t_2	e
30	70	t_2	t_2	a_1	e
42	106	t_2	t_2	a_1	e
66	130	t_2	a_1	t_2	e
82	154	t_2	a_1	e	t_2
136	256	t_2	a_1	t_2	e
148	268	t_2	a_1	t_2	e
172	292	t_2	t_2	e	a_1
196	340	t_2	a_1	e	t_2
220	364	t_2	e	t_2	a_1
256	424	t_2	e	a_1	t_2
268	460	t_2	e	t_2	a_1
316	508	t_2	a_1	t_2	e
344	576	t_2	t_2	a_1	e
368	600	t_2	t_2	e	a_1
452	684	t_2	a_1	t_2	e
542	822	t_2	a_1	t_2	e
706	1058	t_2	t_2	e	a_1

The calculated level structures near the gap are shown in Table I. All the clusters containing more than 17 Si atoms have a highest occupied orbital with t_2 symmetry. The lowest three unoccupied orbitals have symmetries a_1, e, and t_2. The energy spacing for the three lowest conduction-band levels is clearly less than the average level separation and drops below 0.02 eV for the larger clusters we have studied. Dipole transitions from the highest occupied level to any one of the three lowest unoccupied levels are allowed. A lowering of the global symmetry will not lead to forbidden transitions again. Slight changes in surface properties may interchange the three conduction bottom levels, but this will not change the lowest-energy transition to be dipole allowed.

One may ask how the dipole-allowed transition for crystalline microclusters is compatible with the dipole-forbidden transitions in a bulk silicon lattice. However, there is no problem: it is the periodicity which leads to a k-selection rule which renders the dipole matrix element from the valence-band top to any linear combination of conduction-band bottom orbitals zero. One should expect that the oscillator strength goes to zero as the bulk is approached by increasing the cluster size. This is evidenced in Fig. 1, showing the calculated oscillator strength as a function of cluster size. Oscillator strength decreases markedly on approaching the bulk, as expected. Rather wild variations for the three lowest-energy optical transitions, going from one cluster to another, show sensitivity to the detailed structure of the surface. In our calculations the clusters contain all silicon atoms of a rigid Si lattice that fall inside a predetermined radius.

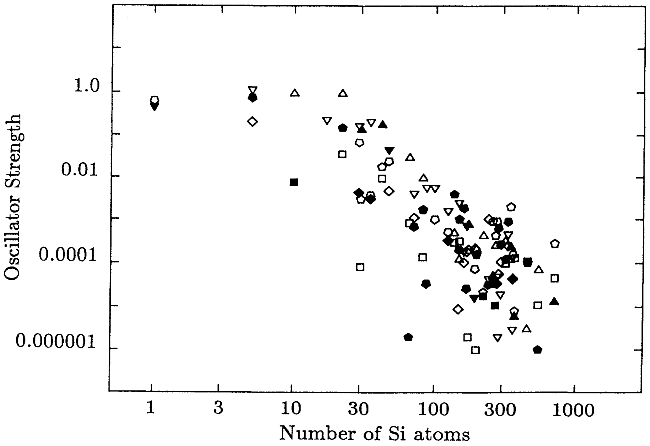

FIG. 1. Oscillator strength vs the number of Si atoms in the cluster. The pentagon refers to transitions involving the a_1 conduction orbital, the square to e, and the triangle to the t_2 symmetry, respectively. Polygons standing on a vertex relate to clusters with an atom at the origin, the others have a tetrahedral interstitial at the origin. Filled symbols refer to the lowest-energy transitions.

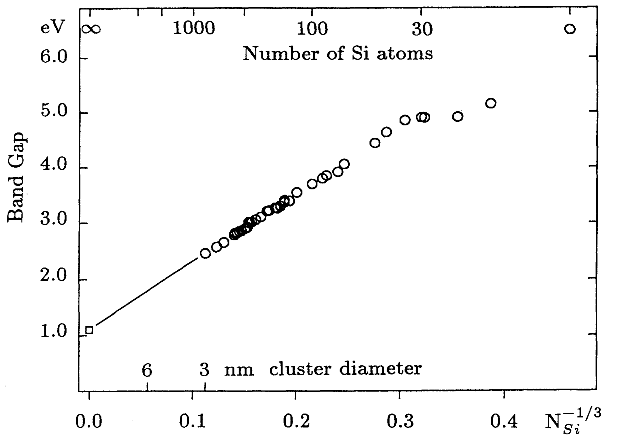

FIG. 2. The calculated band gap, including self-energy correction for clusters containing N_{Si} Si atoms plotted vs $N_{\mathrm{Si}}^{-1/3}$. Dangling bonds at the surface have been hydrogen saturated.

So the variations of oscillator strength trace back to the granularity of the surface.

Unlike the matrix elements, the band gap shows a rather smooth variation with cluster size. Figure 2 shows a plot of band gap versus $N_{\mathrm{Si}}^{-1/3}$ of the calculated clusters with N_{Si} Si atoms. A size-independent self-energy correction as discussed above has been applied. Our largest calculation for a cluster with 706 Si atoms has a radius of 3 nm, corresponding to the smallest clusters of the experimentally reported size range. For the smaller clusters that were accessible to calculations the band gap shows an almost linear behavior as a function of the inverse cluster diameter. The small fluctuations around the linear function are due to the discreteness of the level structure. The linear behavior extrapolates to the bulk Si band gap. The size range between bulk and our calculated cluster covers the energy gaps to be postulated on the basis of the observed inhomogeneously broadened luminescence peaks, both for small particles as well as for porous and reactive ion-etched ("black") silicon.[5] The particular luminescence line shape depends on the particle size distribution obtained by the particular preparation procedure. The calculated oscillator strengths suggest that the smaller particles contribute significantly more to the luminescence than the more coarse particles.

We have calculated electronic properties for a series of hydrogen-saturated silicon clusters ranging from monosilane up to a spherical cluster of 3-nm diameter. The density-functional band gap corrected by a self-energy extrapolates almost linearly to the bulk band gap. The calculated gap covers the spectral range of experimentally observed photoluminescence peaks for the reported size range of nanocrystalline silicon structures. While all three-dimensionally-confined structures are found to have symmetry-allowed transitions across the gap, the oscillator strength is found to markedly increase going from larger to smaller clusters. Thus on a fundamental basis, finely structured silicon appears to be capable of showing a very high photoluminescence in the visible range, as observed experimentally.

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